A NOVEL METHOD FOR THE IMPROVEMENT IN THERMOELECTRIC PROPERTY OF TIN OXIDE THIN FILMS AND ITS APPLICATION IN GAS SENSING

Anuradha S and K. Rajanna*

Department of Instrumentation, Indian Institute of Science,

Bangalore- 560012, INDIA

*E-mail address: kraj@isu.iisc.ernet.in

Abstract - Tin oxide thin film deposited on to glass substrates by the process of DC reactive magnetron sputtering has been used in our work. These films were characterized for their thermoelectric behavior. Further, a novel method has been developed to enhance the Seebeck coefficient of these films. Prior to the oxide film deposition on the glass substrate, thin metal films have been deposited at the two ends of the sample. High conductivity metals such as chromium, silver and copper were used for this purpose. On characterizing these films for their thermoelectric property, a high Seebeck coefficient of 400 μV/^{0}C has been achieved. In addition to this, we also report the results of the gas sensing behavior of a sensor developed using this film which exhibited a maximum response to acetone gas at a relatively low temperature of 110 ^{0}C.

Index terms : Tin oxide, Seebeck coefficient, Gas sensor, Chromium, Acetone.

I. INTRODUCTION

Thermoelectric effect is one of the highly reliable and important working principles that is widely being put into practical applications. Thermoelectric thermometry, thermoelectric generator and thermoelectric refrigeration are the typical applications of the Seebeck effect [1]. The present day research in this field focuses on the development of high seebeck coefficient materials. An enhanced seebeck coefficient is exhibited by materials possessing high electrical conductivity and low thermal conductivity. Metallic oxides have been recognized as good candidates for thermoelectric applications because of their low thermal conductivity, high chemical stability at high temperatures in air, ease of deposition and low toxicity.

Gas sensors have found wide application in industrial production, environmental monitoring, protection, etc. It has been known for a long time that the process of gas adsorption on porous semiconductor surface can change the electrical properties of the surface [2]. Among the sensors investigated and developed, tin oxide based sensors received much attention since they can detect a wide variety of gases with high sensitivity, good stability and also low production cost. However, like other semiconductor gas sensors, SnO_2 sensors should be operated at higher temperatures, which brings about much inconvenience for practical applications and sometimes is even unsafe for detecting combustible gases.

In the present paper, we report the detailed experimental study carried out on the influence of metal thin film on the thermoelectric properties of semiconducting tin oxide film. In addition to this, we also report the results of the gas sensing behavior of a sensor developed using this film which shows a maximum response to the test gas at a relatively low operating temperature.

II. EXPERIMENTAL

a. Deposition of tin oxide film

Tin oxide thin film deposited on a glass substrate has been used as the thermoelectric material in our experiments. Glass was used as the substrate due to its property of high thermal insulation, which is essential for maintaining a temperature gradient along the substrate. The required thin film deposition is done by DC reactive magnetron sputtering.

Glass substrates were thoroughly cleaned by the standard procedure. The cleaned substrates were then placed in the deposition chamber of the sputtering system and SnO_2 film was deposited on to it. A 99.99% pure tin target was used for this purpose. Composition of the SnO_2 films was controlled by controlling the partial pressures of oxygen and argon gases using MKS PR4000 mass flow controllers. The as-deposited film had a thickness in the range of 2000Å to 2500Å. Table 1 shows the optimized deposition parameters for the SnO_2 film.

Table 1: Optimized deposition parameters for tin oxide film

Parameter	Value
Base pressure	1 X 10^{-6} mbar
Working pressure	3 X 10^{-3} mbar
Oxygen : Argon	1: 9
Target to substrate distance	65 mm
Substrate temperature	25^0C
Current density	2.63 mA / cm^2
Deposition rate	200 Å / min

b. Characterization of SnO_2 films:

The tin oxide films prepared were initially tested to ascertain their semiconducting behavior. The sample was placed on a heater and its resistance was measured as the temperature was ramped up from room temperature (26^0C) to 200^0C. Films deposited with O_2: Ar ratio above 1:4 resulted in highly insulating films that were unsuitable for gas sensing applications. Films with O_2: Ar ratio lesser than 9:100 resulted in metallic films that were again unsuitable. Good semi conducting tin oxide films were obtained for O_2: Ar ratio of 1:10.

These samples were then tested for their thermoelectric behavior in a test chamber built in the laboratory (Fig. 1).

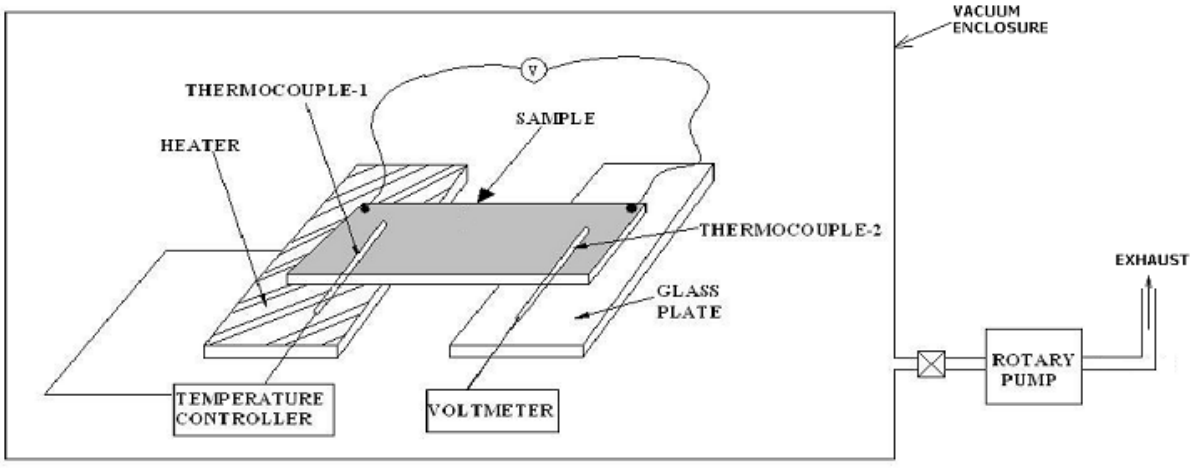

Figure 1. Schematic view of the thermoelectric characterization set-up.

The chamber in which the sample was tested was initially pumped using a rotary pump to a rough vacuum of 1 X 10^{-2} mbar. The difference in temperature at the two ends of the sample was measured by placing two chromel-alumel thermocouples at the ends of the sample. In order to create a temperature gradient along the sample, only one end of the sample was heated leading to the creation of a hot junction and a cold junction. One of the thermocouples measures the temperature at the hot junction of the sample, whereas the other thermocouple measures the temperature at the cold junction. A graph of temperature difference against the measured thermovoltage was plotted and the slope of the curve thus obtained gives the Seebeck coefficient of the film (Fig. 2). The seebeck coefficient of the deposited films was found to be negative confirming to the n-type behavior of tin oxide.

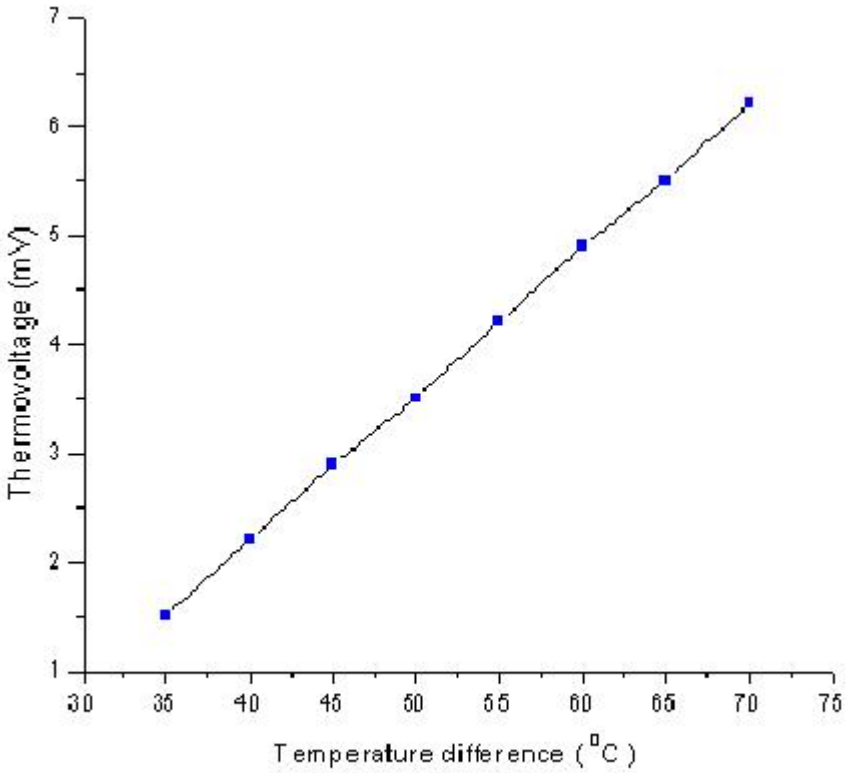

Figure 2. Variation of resistance of SnO_2 film with heater temperature.

The SEM image of the deposited film is shown in Fig. 3. As can be seen, the tin oxide film is non-porous with an average grain size of 400 nm. In all our experiments the thickness of tin

oxide film has been maintained at 2000 Å as films with this thickness were found to have a high seebeck coefficient of ≈185.38 $\mu V/^0C$.

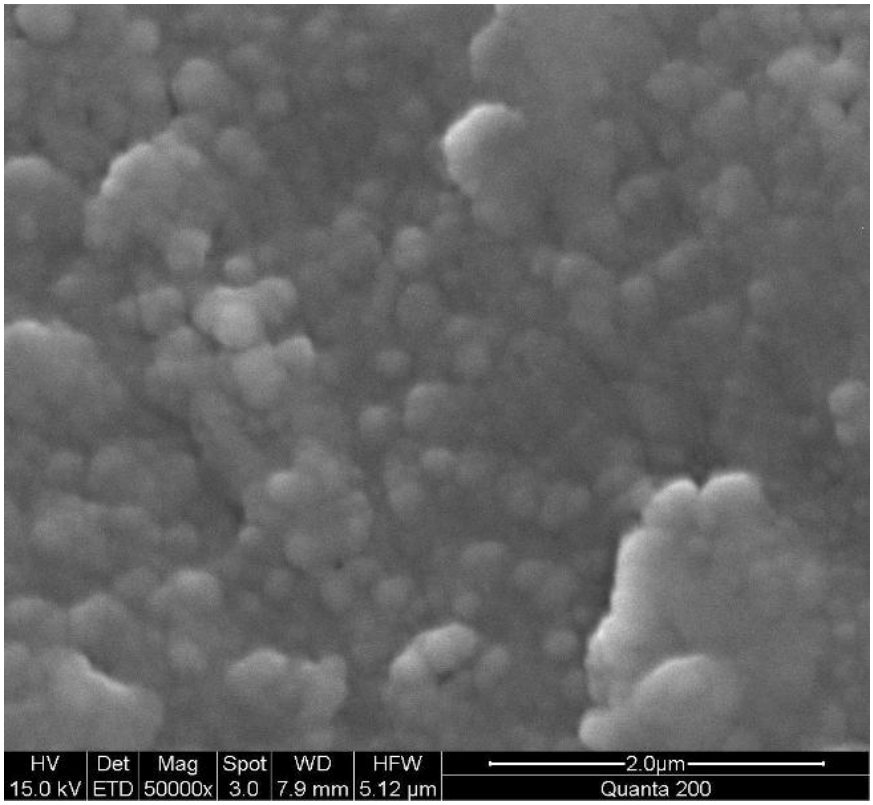

Figure 3. SEM microstructure of the tin oxide film.

c. Improvement of Thermoelectric Property of Tin Oxide Films

As mentioned above, an ideal thermoelectric material should possess large Seebeck coefficients, high electrical conductivity and low thermal conductivity [3]. High electrical conductivity is necessary in order to minimize Joule heating, while a low thermal conductivity helps to retain heat at the junctions and maintain a large temperature gradient. In metals, the ratio of the thermal conductivity to electrical conductivity is a constant (Wiedemann-Franz-Lorenz law) and it is not possible to reduce one, while increasing the other. Most metals possess Seebeck coefficients of 10 $\mu V/^0C$ or less, which are uneconomical for a large number of applications. In semiconductors the ratio of the thermal conductivity to electrical conductivity is greater than in metals owing to their poorer electrical conductivity. This ratio can be decreased (i.e., the electrical conductivity can be increased) if the thermoelectric material is alloyed with an isomorphous element or compound [4].

In our work, a novel method has been used to enhance the electrical conductivity of the semi conducting oxide and in turn the Seebeck coefficient of the SnO_2 film. High conductivity metal thin films in the form of strips have been deposited at either ends of the glass substrate prior to the oxide film deposition (Fig. 4). This was followed by the deposition of tin oxide film by DC reactive magnetron sputtering technique.

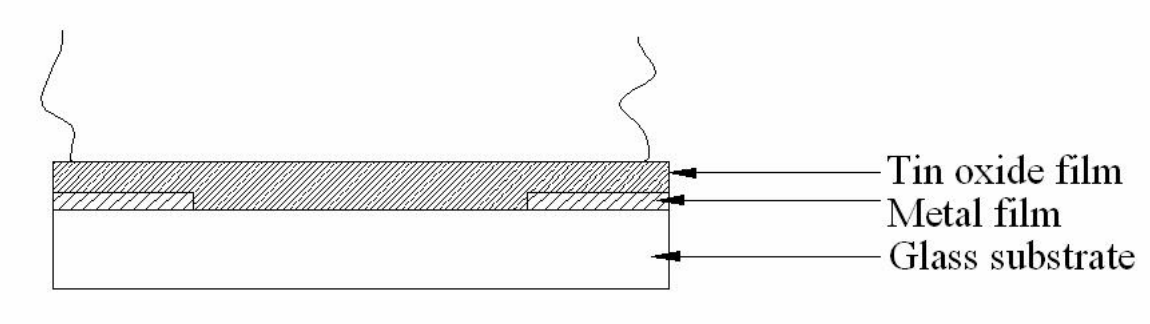

Figure 4. Cross-sectional view of the sample with metal films.

The dimensions of the substrate used are 3.65cm X 2.9cm and the surface area covered by the metal films on either ends is 2.9cm X 0.85cm. The separation between the metal films has been optimized for the maximum seebeck coefficient of the oxide film. We have used high electrical conductivity metals namely silver, chromium and copper for the purpose of increasing the overall thermoelectric property of the tin oxide film. Prior to the deposition of oxide film, the substrates were thoroughly cleaned by the standard procedure and the metal films were deposited on to the two ends of the substrate by the process of DC magnetron sputtering. The thickness of the deposited metal thin films has been maintained at 2000 Å. Tin oxide films were then deposited on to these samples by the process of DC reactive magnetron sputtering with the deposition parameters mentioned in table 1. Double enameled copper wires were attached to these samples in order to facilitate electrical measurements. The samples were characterized for their thermoelectric behavior using the procedure mentioned earlier. In order to demonstrate the applicability of improvement in thermoelectric property of the tin oxide films, we have fabricated a gas sensor, the details of which are discussed in the following section.

d. Sensor fabrication

Tin oxide and platinum represent a proven combination in catalysis and bring several reactive gases within the range of the thermoelectric mechanism even at low temperatures [2]. In order

to create the necessary temperature gradient along the sensor substrate, platinum catalyst was deposited (in the form of particles) on half the surface of the oxide film (Fig. 5), such that combustion of the reducing gas takes place only on the catalyst. Deposition of platinum has been performed by DC magnetron sputtering of a Pt target. Thickness of the deposited platinum film has been maintained at 10 nm. Double enameled copper wires were attached to the ends of the sample in order to facilitate electrical measurements.

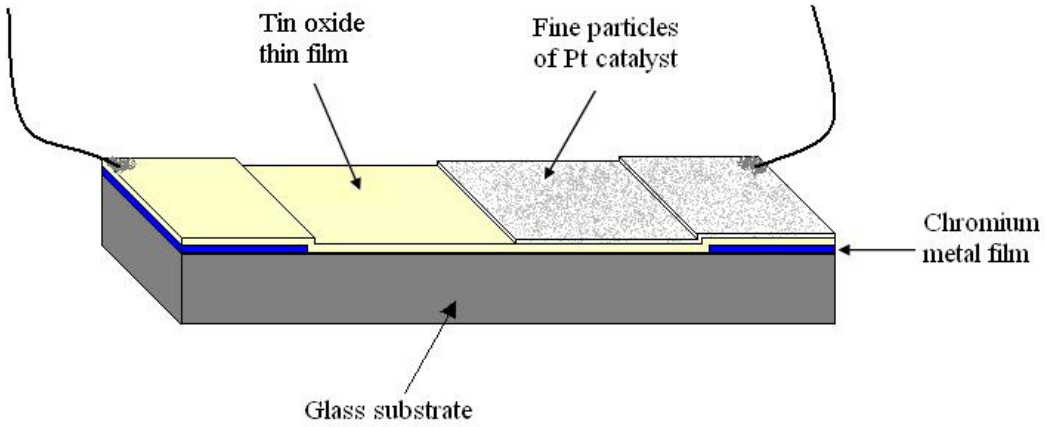

Figure 5. Schematic diagram of the developed gas sensor.

e. Sensor Testing

The sensor has been tested for its gas sensing abilities in an in-house made testing set-up. The sensor was placed on a heater, which in turn was connected to a temperature controller. The sensor-heater element was placed inside the stainless steel gas-testing chamber. The chamber was initially evacuated using a rotary pump to a rough vacuum of 2×10^{-3} mbar. The required temperature of operation was set using the temperature controller. The test gases were injected into the chamber via a syringe through the inlet. The measurements were performed in the temperature range of 80 to 160^0C. A chromel-alumel thermocouple placed in close proximity of the sensor was used to measure the working temperature of the sensor. The output voltage was measured by attaching the double enameled copper wires on the sensor to a multimeter outside the system via a feed through.

III. RESULTS AND DISCUSSION

a. Thermoelectric properties of tin oxide film

Tin oxide is a wide gap (3.6 eV) n-type semiconductor, whose electrical conductivity is due to the non-stoichiometric composition as a result of oxygen deficiency. In our experiments, we have characterized tin oxide thin film deposited on a glass substrate for its thermoelectric behavior. In addition to this, samples with tin oxide thin films deposited with metal films beneath them (on either ends) have also been characterized. Fig. 6 shows the variation of thermoelectric voltage with temperature gradient for tin oxide films with and with out metal film.

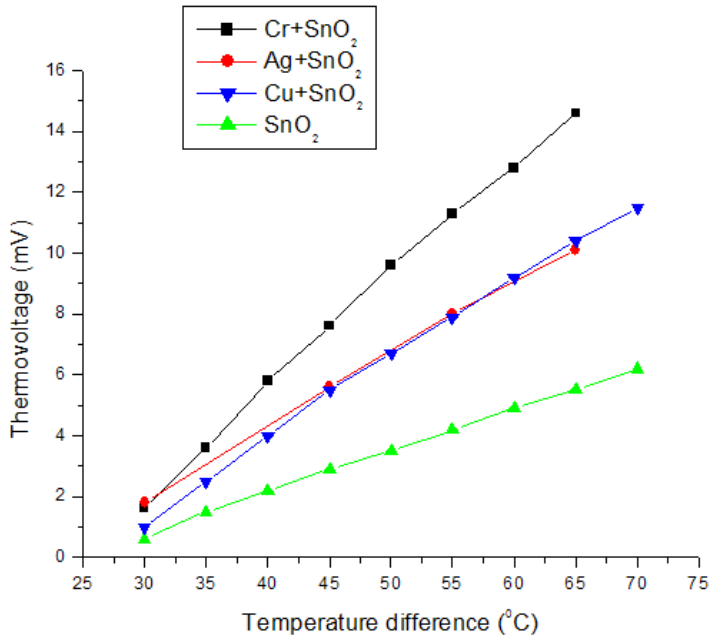

Figure 6. Variation of the thermovoltage with temperature for SnO_2 thin film with different metal films and without metal film.

As can be seen, the samples with chromium metal films + tin oxide exhibited a marked increase in the thermoelectric property. The observed increase in the seebeck co-efficient of the samples can be attributed to the increase in the number of charge carriers due to the metal

film deposition. The Seebeck coefficients of the samples with the deposited metal films have been tabulated in Table 2.

Table 2: Seebeck coefficient of the deposited samples with metal films.

Sample Number	**Composition of thermoelectric film**	**Seebeck Coefficient ($\mu V/^0C$)**
1	SnO_2	185.38
2	SnO_2 + Cr	323.68
3	SnO_2 + Cu	149.01
4	SnO_2 + Ag	225.24

In addition to this, we have observed that the seebeck coefficient of the samples with metal films was negative indicating that the dominant contributing factor to the thermoelectric effect is the tin oxide film.

Among the metals tested, samples with chromium films exhibited an overall seebeck coefficient of 400 $\mu V / {}^0C$. The SEM micrograph of the chromium metal film shows evenly distributed grains on the substrate with an approximate grain size of 250 nm (Fig. 7).

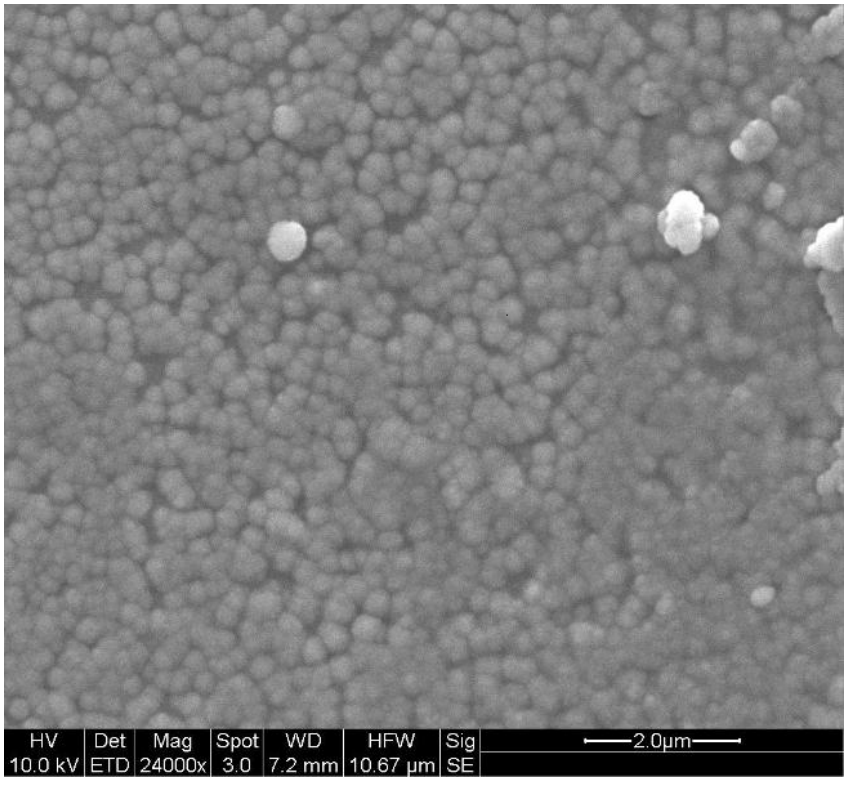

Figure 7. SEM microstructure of the chromium film.

Among the metals used for the purpose of increasing the thermoelectric property of SnO_2 films, chromium has the optimum combination of high electrical conductivity and low thermal conductivity (Table 3).

Table 3: Electrical and thermal conductivity data of the metals used.

Metal used	**Electrical Conductivity ($m^{-1}\Omega^{-1}$)**	**Thermal Conductivity ($Wm^{-1}K^{-1}$)**
Chromium	7.74×10^6	93.9
Copper	59.6×10^6	401
Silver	63×10^6	429

b. Gas sensing properties of the sensor

As mentioned above, we initially carried out studies to test for the suitability of SnO_2 film for thermoelectric gas sensing applications. In addition to this, sensors were also fabricated using SnO_2 + metal film along with the deposition of platinum catalyst on half the surface of the sensing layer. The result of gas sensing behavior of theses sensors has been presented in the following section.

b.i. Response of the sensor without metal films

Sensors developed with only tin oxide as the sensing film were tested for their response to varied concentrations of acetone gas in the ambient environment. During each test trial, a known concentration of the test gas was allowed into the chamber and the operating temperature of the sensor was ramped up from 110 ^{0}C to 150 ^{0}C. As a result of the catalytic activity of platinum, reduction of acetone takes place on the surface of the tin oxide film covered with platinum catalyst. The resulting heat of reaction leads to the development of a temperature gradient along the surface of the sensor. Due to the thermoelectric property of tin oxide film, a voltage was thus generated across the surface of the sensor. Fig. 8 shows the response of the sensor to two different concentrations of acetone gas. The maximum response of the sensor to the tested gas is obtained at a temperature of 145 ^{0}C.

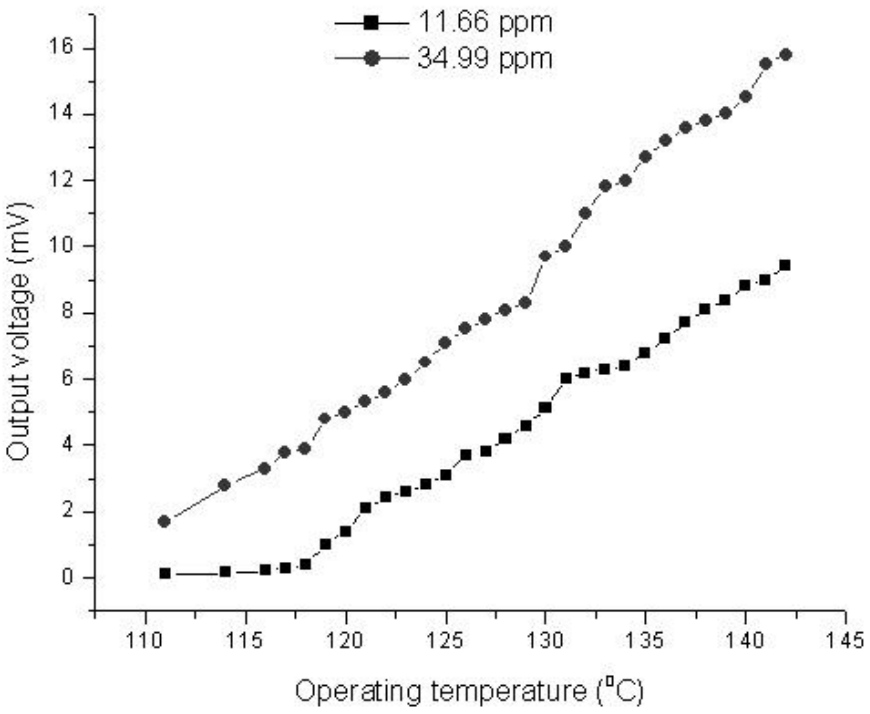

Figure 8. Response of the gas sensor to varying concentrations of acetone.

b.ii. Response of the sensor with metal films

A comparison of the response of the sensor with and without metal films to acetone gas is shown in Fig. 9. It is evident from this figure 9, that the temperature of maximum response is reduced considerably in sensors with additional metal films. This increase in the output response of the sensor to acetone at a lower temperature can be attributed to an increase in seebeck coefficient of the sensing film. A smaller temperature gradient across the sample produces a high measurable output voltage even at lower temperatures. Further results of the gas sensing abilities of this sensor have been reported elsewhere [5].

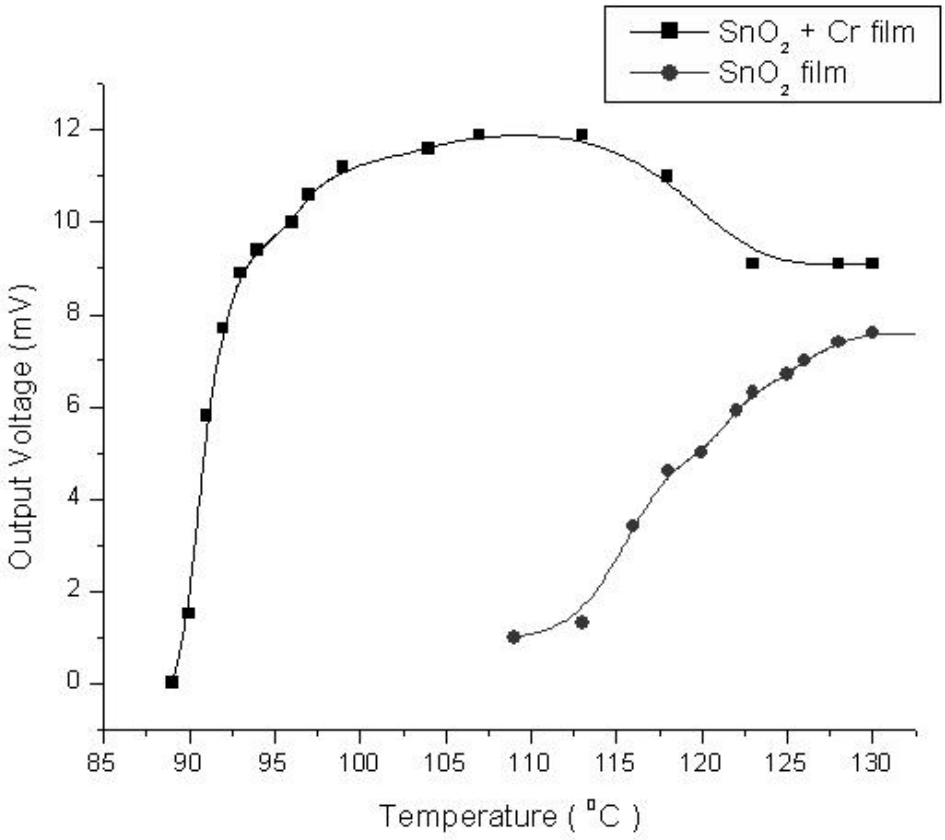

Figure 9: Comparison of the sensor response with and without metal films to acetone gas.

As mentioned earlier, in addition to chromium, metals like silver and copper were also used to enhance the seebeck coefficient of the gas sensitive tin oxide film. A comparison of the response of the gas sensors with different metal films to acetone has been depicted in Fig. 10. The sensors with Cu + SnO_2 and Ag + SnO_2 films also demonstrate a good sensitivity to ppm concentrations of acetone gas. It can be noted from the above figures that the magnitude of response of the sensors with copper and silver films to acetone gas is low compared to that of sensor with chromium film. This can be attributed to the high seebeck coefficient of the tin oxide + chromium films.

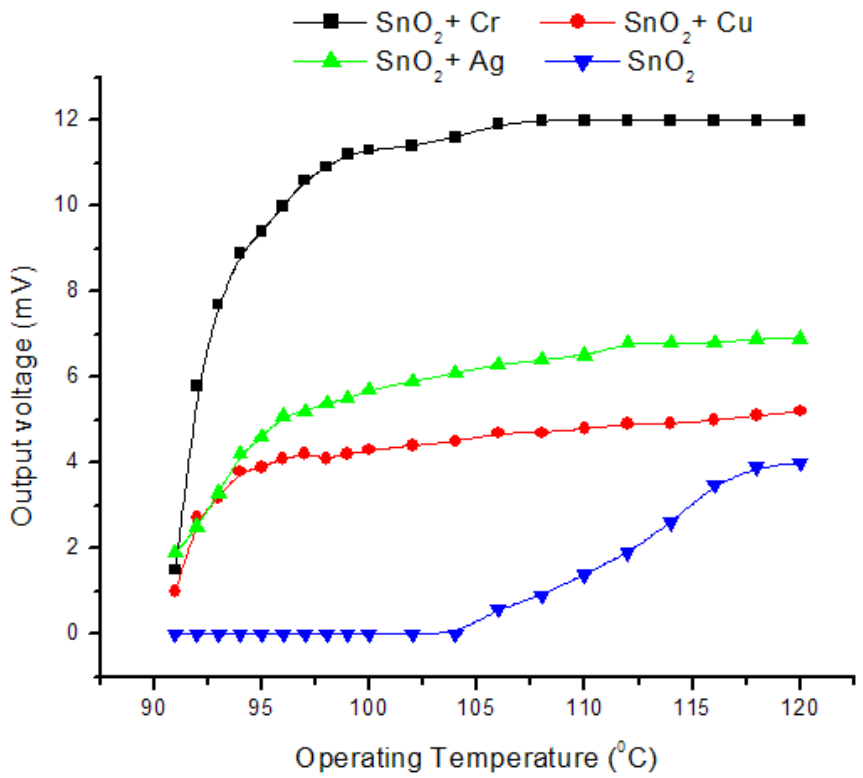

Figure 10. Comparison of the response of the gas sensors with and without metal films to 28 ppm of acetone.

IV. CONCLUSIONS

A novel method of increasing the seebeck coefficient of tin oxide films has been successfully implemented. Tin oxide thin films with chromium film deposited on either ends of the substrate exhibited a seebeck coefficient as high as 400 $\mu V/^0C$. The applicability of this film for gas sensing has also been demonstrated and the sensors with chromium and tin oxide films showed a maximum response to acetone at a relatively low temperature of 110 ^0C.

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